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## PATENT ABSTRACTS OF JAPAN

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## (54) IMAGE FORMING METHOD

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide an image forming method by which a sharp character can be formed and an image with good black solid density and little fog can be formed.

SOLUTION: This image forming method includes a process to form a toner layer on a toner carrying body facing an electrostatic latent image holding body and a process to develop an electrostatic latent image on the electrostatic latent image holding body. The coating amt. of the toner layer per unit area on the toner carrying body is  $w/p=0.2$  to 0.8, wherein (w) is the weight of toner coating (mg) per 1cm<sup>2</sup> of the toner carrying body and p is the toner density (g/cm<sup>3</sup>). The surface roughness Ra of the toner carrying body is  $\leq 1.8$ , and the toner contains at least toner particles and an inorg. fine powder. The inorg. fine powder is treated with a silane coupling agent and has 60-180g/l bulk density and pH 4.5 to 8.5.

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**CLAIMS**


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**[Claim(s)]**

[Claim 1] The amount of coats per unit area of a toner layer which forms a toner layer on electrostatic latent-image support and toner support which countered, and is formed on toner support in an image formation method of having a production process which develops an electrostatic latent image on electrostatic latent-image support is the toner coat weight (mg) per two 1cm of  $w/\rho = 0.2 - 0.8w$ ; toner support surfaces.

$\rho$ ; toner true density (g/cm<sup>3</sup>)

\*\*\*\*\* — an image formation method that it is set up like, and average roughness Ra of this toner support surface is 1.8 or less, this toner has a toner particle and non-subtlety fine particles at least, these non-subtlety fine particles are processed by silane coupling agent, and bulk density is characterized by pH being 4.5–8.5 in l. in 60–180g /.

[Claim 2] An image formation method according to claim 1 characterized by filling following condition  $-5X+35 \leq Y \leq -25X+1803.5$   $\leq X \leq 6.5$  when particle size distribution of this toner set to Y (%) number% of pieces 3.17 micrometers or less of number criteria which asked for a weight mean diameter (D4) from X (micrometer) and number distribution.

[Claim 3] An image formation method according to claim 1 or 2 characterized by carrying out 0.05–3 weight section addition of these non-subtlety fine particles to this toner particle 100 weight section.

[Claim 4] An image formation method according to claim 1 to 3 characterized by containing silicone oil or a silicone varnish 20 to 90% of the weight in this toner, and bulk density containing the second non-subtlety fine particles whose specific surface area is 0.01–50m<sup>2</sup>/g in ml in 0.2–0.8g /.

[Claim 5] An image formation method according to claim 4 characterized by carrying out 0.02–1 weight section addition of the second non-subtlety fine particles to this toner particle 100 weight section.

[Claim 6] An image formation method according to claim 1 to 5 characterized by bulk density processed by silicone oil or silicone varnish after silane coupling agent processing containing the third non-subtlety fine particles whose specific surface area is 80–140m<sup>2</sup>/g in l. in 30–60g /in this toner.

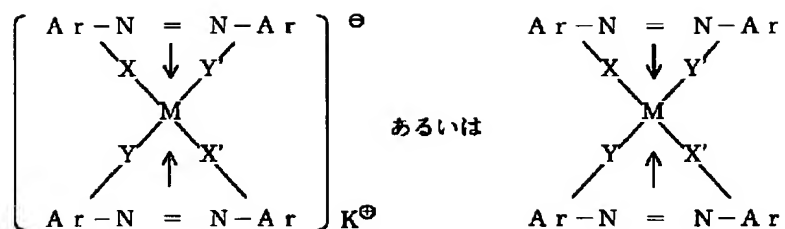
[Claim 7] An image formation method according to claim 6 characterized by carrying out 0.05–3 weight section addition of the third non-subtlety fine particles to this toner particle 100 weight section.

[Claim 8] An image formation method according to claim 1 to 7 characterized by containing the magnetic substance and a silicon atom containing 0.2 to 2.0% of the weight to this magnetic substance in this toner particle.

[Claim 9] An image formation method according to claim 8 characterized by for this toner particle containing binding resin and the magnetic substance at least, and carrying out 70–150 weight section content of this magnetic substance to this binding resin 100 weight section.

[Claim 10] An image formation method according to claim 1 to 9 characterized by containing an organometallic compound shown by the following formula as an electric charge control agent in this toner particle.

[Formula 1]



[M: Fe, Mn, Al, Ni, Co, Cr, Sc, Ti, V

Ar: フェニル基, ナフチル基,

置換基 (ニトロ基, ハロゲン基, カルボキシル基, アニリド基,

炭素数 1~18 のアルキル基あるいはアルコキシ基) を有する

フェニル基あるいはナフチル基を示す。

X, X', Y, Y' : -O-, -NH-, -NR- (R は炭素数 1~4 の

アルキル基) を示す。

K<sup>⊕</sup>: H<sup>⊕</sup>, Na<sup>⊕</sup>, K<sup>⊕</sup>, NH<sub>4</sub><sup>⊕</sup>, 脂肪族アンモニウムイオン、あるいは

これらいずれかの混合イオンを示す。]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the image formation method like a xerography and an electrostatic recording method.

[0002]

[Description of the Prior Art] Conventionally, many methods are learned as a xerography. After generally use photoconductivity material, forming an electric latent image on image support (photo conductor) with various means, developing negatives with a toner, using this latent image as a visible image subsequently and imprinting a toner image to imprint material, such as paper, if needed, a toner image is established on imprint material with heat, a pressure, etc., and a duplication is obtained.

[0003] In recent years, the device using a xerography is becoming a large number, such as a printer and facsimile, in addition to the conventional copying machine.

[0004] For example, as for printer equipment, that LED or a LBP printer had become the mainstream of the latest commercial scene, and was [ that ] 240,300dpi high resolution, i.e., conventionally, as a direction of technical is being set to 400,600,800dpi. Therefore, in connection with this, the high definition has been required more also for the development method. Moreover, advanced features are progressing also in the copying machine, therefore it is progressing towards digitization. Since this direction has the main method of forming an electrostatic-charge image by laser, it is progressing in the high resolution direction too, and high resolving and a high definition development method have been required like a printer also here. For this reason, diameter-ization of a granule of a toner is progressing and the toner with a small particle size of specific particle size distribution is proposed in JP,1-112253,A, JP,1-191156,A, JP,2-214156,A, JP,2-284158,A, JP,3-181952,A, and JP,4-162048,A.

[0005] On the other hand, as a development method, the 1 component development method is preferably used from a viewpoint of the miniaturization of a printer, facsimile, etc., and lightweight-izing. The jumping development methods (JP,58-32375,B etc.) which develop negatives also in it by forming the toner thin layer which sets and arranges toner support and electrostatic latent-image support, and does not contact [ support ] latent-image support on toner support in a certain fixed gap, and impressing mutual electric field between toner support and latent-image support further are used preferably.

[0006] However, also in this development method, in order to form the further highly minute image, the method of making a toner develop faithfully according to the latent image on electrostatic latent-image support is examined. For example, although the direction which reduces the weight per unit area is a method used suitable for the direction of highly-minute-izing of image quality, the present condition is that generating of solid \*\*\*\*\* and fogging is seen when an above-mentioned minor diameter-ized toner is used, and the image to satisfy is not obtained.

[0007] In order to be able to attain the highly minute image more than before and to attain the image formation method that solid black concentration can form a high image with little fogging, fluid improvement is fundamentally desired as a toner.

[0008] The non-subtlety fine particles which performed hydrophobing processing by JP,5-66608,A, JP,4-9860,A, etc. as a way stage which secures the fluidity of a toner, or after carrying out hydrophobing processing, the method of carrying out concomitant use addition is learned [ pulverized coal / hydrophobing processing inorganic pulverized coal and / silicone oil processing inorganic ] for addition or JP,61-249059,A, JP,4-264453,A, and JP,5-346682,A in the non-subtlety fine particles further processed by silicone oil etc.

[0009] However, even if it used the toner using such technique, still maintaining the balance of alphabetic character Sharp nature, solid black concentration, and fogging suited the difficult condition.

[0010]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the image formation method solid black concentration able to form a sharp alphabetic character and to form a good image with little fogging.

[0011] Moreover, the purpose of this invention is to offer the image formation method which can form the alphabetic character which attains the above-mentioned purpose and does not have an inside omission.

[0012]

[Means for Solving the Problem and its Function] This invention attains the aforementioned purpose by the following configuration.

[0013] That is, for this invention, the amount of coats per unit area of a toner layer which forms a toner layer on

electrostatic latent-image support and toner support which countered, and is formed on toner support in an image formation method of having a production process which develops an electrostatic latent image on electrostatic latent-image support is the toner coat weight (mg) per two 1cm of  $w/\rho = 0.2 - 0.8w$ ; toner support surfaces.  $\rho$ ; toner true density (g/cm<sup>3</sup>)

\*\*\*\*\* — it is set up like, and the average roughness  $R_a$  of this toner support surface is 1.8 or less, it has a toner particle and non-subtlety fine particles at least, these non-subtlety fine particles are processed by silane coupling agent, and this toner is related with an image formation method that bulk density is characterized by pH being 4.5–8.5 in l. in 60–180g /.

[0014] About a development method, when  $w/\rho$  is smaller than 0.2, solid black concentration is not secured enough, and it is not desirable. When  $w/\rho$  is larger than 0.8, spilling increases to an alphabetic character periphery, a sharp alphabetic character is not formed, and it is not desirable. Moreover, when the average surface roughness  $R_a$  of toner support is larger than 1.8, a sharp alphabetic character is not formed and it is not desirable. It is the case where  $R_a$  is 1.5 or less more preferably. So, it is necessary for attaining the purpose of this invention to have development conditions like this invention.

[0015] It is required to combine a toner containing non-subtlety fine particles characterized by being processed by silane coupling agent, and for bulk density being 60–180g/l., and pH being 4.5–8.5 to still such development conditions.

[0016] When bulk density of these non-subtlety fine particles is smaller than l. 60g /, sufficient fluidity for a toner cannot be given, a uniform toner coat layer is not formed in a system which makes a toner layer like this invention a thin layer, and sufficient solid black concentration is not obtained. When bulk density is larger than l. 180g /, a fluid fall of a toner arises similarly, a uniform toner coat layer is not formed in a thin layer system like this invention, and sufficient solid black concentration is not obtained.

[0017] Furthermore, a thing of a neutral region has [ a pH value of non-subtlety fine particles added at this time ] good orientation in the Sharp nature of an alphabetic character, image concentration, and an omission in an alphabetic character. Generally, by binding resin etc., electric charge control agent \*\*\*\* has the electrification nature of negative or a positive one direction, and a toner particle carries out appearance layout. Although it is not clear in that mechanism to add non-subtlety fine particles to which a charge from which electrification ability of a toner is puffed up too much, or is made to be subtracted to this electrification direction is made to give, in a development method of a thin layer coat system which is used especially by this invention, it is easy to produce evil. For example, in the case of a negative electrification nature toner, if pH is smaller than 4.5, aggravation of spilling will be seen and the Sharp nature of an alphabetic character will fall. If larger than 8.5, a fall of solid black concentration and aggravation orientation of an omission in an alphabetic character will be seen. Ranges used more preferably are 5.0–8.0.

[0018] In addition, toner true density of this invention used data measured with a Shimadzu dry type automatic density meter "the AKYU pick 1330."

[0019] The center line average of roughness height ( $R_a$ ) is measured using a surface roughness measuring instrument (surfboard coder SE-30H, Kosaka Laboratory, Ltd.) based on JIS surface roughness (BO601). Specifically, center line granularity ( $R_a$ ) says what expressed with a micro meter (micrometer) a value calculated by the following formula, when the direction of the X-axis and longitudinal magnification is expressed with a Y-axis and it expresses a granularity curve with  $y=f(x)$  for a center line of this sampling portion by sampling a measurement length  $a$  2.5mm portion in the direction of that center line from a granularity curve.

[0020]

[Equation 1]

$$R_a = \frac{1}{a} \int_0^a |f(x)| dx$$

[0021] As toner support used for this invention, cylindrical [ which consists, for example of stainless steel, aluminum, etc. ], or a belt-like member is used preferably. Moreover, coats, such as a metal and resin, may be carried out for the surface if needed, and the coat of the resin which distributed particles, such as resin metallurgy groups, carbon black, and an electrification control agent, may be carried out.

[0022]

[Embodiment of the Invention] As non-subtlety fine particles used by this invention, a silica, an alumina, a titania, etc. can be used and, especially as for the original object silica before silane coupling agent processing, silicic-acid pulverized coal is used good.

[0023] Although the so-called both of the wet silica manufactured from the dry type silica called the so-called dry process or the fumed silica generated by vapor phase oxidation of a silicon halogenide, water glass, etc. of silicic-acid pulverized coal are usable, few dry type silicas of manufacture remnants, such as  $\text{Na}_2\text{O}$  and  $\text{SO}_3^-$ , with few [ and ] silanol groups in the interior of the surface and silica pulverized coal are more desirable. Moreover, in a dry type silica, by using other metal halogenated compounds, such as an aluminum chloride and a titanium chloride, with a silicon halogenated compound in a manufacturing process, it is also possible to obtain the compound pulverized coal of a silica and other metallic oxides, and they are also included.

[0024] As a silane coupling agent, for example Hexamethyldisilazane, a trimethyl silane, A trimethyl KURORU silane, a trimethyl ethoxy silane, a dimethyl dichloro silane, Methyltrichlorosilan, an allyl compound dimethyl KURORU silane, an allyl compound phenyl dichloro silane, A benzyl dimethyl KURORU silane, bromine methyl dimethyl

KURORUSHIRAN, alpha-KURORU ethyl trichlorosilan, beta-KURORU ethyl trichlorosilan, KURORUMECHIRU dimethyl KURORUSHIRAN, the Tori ORGANO silyl mercaptan, A trimethylsilyl mercaptan, Tori ORGANO silylacrylate, Vinyl dimethyl acetoxysilane, dimethyl diethoxysilane, dimethyl dimethoxysilane, Diphenyl diethoxysilane, hexa methyl disiloxane, 1, 3-divinyl tetramethyl disiloxane, The dimethylpolysiloxane containing the hydroxyl group combined with the silicon atom addressed to one piece, respectively etc. is mentioned to the unit which has 12 siloxane units from per [ 2 ] 1 and 3-diphenyl tetramethyl disiloxane and molecule, and is located in an end.

[0025] Silane coupling agent processing of the above-mentioned pulverized coal can be processed by methods, such as dry type processing to which the silane coupling agent which evaporated pulverized coal to what was made into the shape of a cloud by churning etc. is made to react, or a wet method which distributes pulverized coal in a solvent and carries out the dropping reaction of the silane coupling agent. Although a dry type approach is used preferably even especially in inside, it is not limited to this.

[0026] The method of making particles condense as a method of raising bulk density according to the reaction condition at the time of generating a silicon halogenide for silicic-acid pulverized coal or operations (a Henschel mixer, mix Mahler, etc.) behind mechanical before carrying out silane coupling agent processing is mentioned.

[0027] The specific surface area by the nitrogen adsorption measured with the BET adsorption method has [ the non-subtlety fine particles used by this invention ] the especially desirable thing of the range of 150-400m<sup>2</sup>/g more than 100m<sup>2</sup>/g.

[0028] Moreover, as for the non-subtlety fine particles of this invention, it is desirable to carry out 0.05-3 weight section addition to the toner particle 100 weight section.

[0029] In this invention, pH measurement is performed using the pH meter which used the glass electrode. Methanol 50cm<sup>3</sup> are added for 4g of samples for a beaker, a sample is wet, 3 is added further 50cm<sup>3</sup> of pure water, and it is made to fully agitate in a homomixer. pH is measured after that.

[0030] The bulk density of the non-subtlety fine particles of this invention measured according to the following procedures using shaking measurement-of-specific-gravity machine KRS-406 (made in the Kuramochi science equipment factory).

[0031] \*\* Supply fine particles to attached 150ml measuring cylinder, and cut the fine-particles upper part by rubbing.

[0032] \*\* Weigh precisely to 0.01 the weight W of the sample put into the cylinder.

[0033] \*\* A shaking measurement-of-specific-gravity machine performs tapping (conditions: a part for fall height [ of 6cm ], and 70 tapping speed/, 1250 counts of tapping), and read the fine-particles capacity V at that time to 1ml unit.

[0034] \*\* Ask for bulk density A by the degree type.

[0035]

Bulk density  $A = (W/V) \times 1000$  (g/l.)

[0036] When number% of pieces 3.17 micrometers or less of the number criteria which asked for the weight mean diameter (D<sub>4</sub>) from X (micrometer) and number distribution are set to Y (%), the particle size distribution of the toner used for this invention are more preferably used, although what is following condition  $-5X+35 \leq Y \leq -25X+1803.5 \leq X \leq 6.5$  attains the purpose of this invention. It increases [ in the case of  $Y > -25X+180$  / a fogging phenomenon ] about particle size distribution and is not desirable. In the case of  $Y < 5X+35$ , the Sharp nature of a character outline is not inferior and desirable. In the case of  $D_4 < 3.5$ , image concentration falls remarkably and is not desirable. It becomes impossible for the Sharp nature of a character outline to be inferior [ in the case of ] and satisfied in the case of  $D_4 > 6.5$ . The range used more preferably is the case of  $-5X+35 \leq Y \leq -10X+804.5 \leq X \leq 6.5$ .

[0037] As for the electrolytic solution, measurement of the particle size distribution of the toner of this invention prepares a NaCl aqueous solution 1% using the 1st class sodium chloride using Coulter counter TA-II or a coal tar multi-sizer (coal tar company make). For example, ISOTON R-II (made in coal tar scientific Japan) can be used. as a measuring method — the inside of 100-150ml of said electrolysis aqueous solutions — as a dispersant — a surfactant — 0.1-5ml of alkylbenzene sulfonate is added preferably, and 2-20mg of test portions is added further. It computed a volume integral cloth and number distribution by the electrolytic solution which suspended the sample having performed distributed processing for about 1 - 3 minutes with the ultrasonic distribution vessel, and having measured the volume of a toner 2 micrometers or more, and the number with said measuring device, using 100-micrometer aperture as an aperture. And it asked for the rate of 3.17 micrometers or less of the number criteria searched for from the weighted mean particle size (D<sub>4</sub>: let the median of each channel be the central value for every channel) of weight criteria and number distribution which were searched for from the volume integral cloth concerning this invention.

[0038] Content of silicone oil or the silicone varnish is carried out further at the toner of this invention 20 to 90% of the weight (preferably 30 - 80 % of the weight). Bulk density 0.2-0.8g (preferably 0.25-7g/(ml))/ml And the second non-subtlety fine particles characterized by specific surface area being 0.01-50m<sup>2</sup>/g (preferably 0.5-30m<sup>2</sup>/g) It is desirable to add suitably in the range of the 0.02 - 1.0 weight section to the toner particle 100 weight section from a viewpoint which falls out among an alphabetic character and prevents drum welding, filming, etc.

[0039] The thing of 1,500 to 100,000 centistokes has [ the thing of 50 to 200,000 centistokes / the thing of further 500 to 150,000 centistokes ] the thing of further 3,000 to 80,000 centistokes still more desirable [ the above-mentioned silicone oil or a silicone varnish / the viscosity in 25 degrees C ]. In less than 50 centistokes, while particle-izing of a lot of silicone oil / silicone varnishes is difficult, there is no stability in a particle and there is

orientation for image quality to deteriorate, with heat and mechanical stress. Particle-ization tends to become difficult when exceeding 200,000 centistokes.

[0040] Especially as silicone oil used, dimethyl silicone oil, methylphenyl silicone oil, alpha-methyl-styrene denaturation silicone oil, KURORU phenyl silicone oil, fluorine denaturation silicone oil, etc. are desirable, for example. As a silicone varnish, a methyl silicone varnish, a phenylmethyl silicone varnish, etc. can be mentioned, for example. As the method of silicone oil / silicone varnish treated, the silica pulverized coal, and the silicone oil / silicone varnish processed, for example by the silane coupling agent may be directly mixed using mixers, such as a Henschel mixer, and the method of spraying silicone oil / silicone varnish on the silica pulverized coal used as the base may be used. Or after making a suitable solvent dissolve or distribute silicone oil / silicone varnish, the method of adding silica pulverized coal, mixing and removing a solvent may be used.

[0041] The 500ml container was made to carry out natural fall of the bulk density of the second non-subtlety fine particles of this invention from the upper part, and the portion which rose from the container measured whatg grinding OFF goes into a container, and it expressed with the value of [g/ml].

[0042] As for the toner of this invention, it is still more desirable to have the third non-subtlety fine particles. this - the third non-subtlety fine particles are combining with the first and second non-subtlety fine particles, and the evaluation balance of concentration, fogging, and an inside omission improves more, and has an effect also to drum welding prevention further. The third non-subtlety fine particles here consist of inorganic compounds which have the same constituent nature as the first non-subtlety fine particles of this invention, and the oxide pulverized coal of a silica or titanium is used especially preferably.

[0043] Also in it, what was processed with silicone oil or a silicone varnish is more desirable, and the third non-subtlety fine particles are used, after processing silica pulverized coal by the silane coupling agent.

[0044] After performing a silane coupling reaction and vanishing a silanol group by the chemical bond as a first stage reaction as processing conditions for silica pulverized coal, it is characterized by forming a hydrophobic thin film in the surface with silicone oil or a silicone varnish as a second stage reaction.

[0045] The silane coupling agent used for this invention can use what is used for the first inorganic pulverized coal of this invention, and the same thing.

[0046] The art of a silane coupling agent is processed by the same method as the first non-subtlety fine particles except there being nothing in \*\*\*\* about the processing which raises bulk density.

[0047] The same material as what is used for the second non-subtlety fine particles may be used for the material used for silicone oil or silicone varnish treated. Although the method same also as an art is mentioned, the method which the rise of bulk density cannot produce easily, for example, the method using a sprayer, is preferably used by condensation of pulverized coal etc. by processing also in it. However, it is not limited to this.

[0048] It is good to the pulverized coal 100 weight section 1 - 40 weight section and for a silane coupling agent to carry out 5-30 weight section processing preferably. the throughput of silicone oil or silicone varnish solid content - the pulverized coal 100 weight section -- receiving -- 1 - 23 weight section -- 5 - 20 weight section is preferably good.

[0049] If there are too few silane coupling agents, good solid black concentration will not be obtained, but if many [ too ], faults, such as fogging generating, will arise. If there are too few amounts of silicone oil or a silicone varnish, good solid black concentration and an inside omission improvement effect will not be seen, but if many [ too ], faults, such as fogging generating, will arise.

[0050] As a characteristic value of the above-mentioned processing silica pulverized coal, the specific surface area of bulk density by the nitrogen adsorption which l. is desirable in 30-60g /, is a 35-55g [/l. ] thing more preferably, and was measured with the BET adsorption method from the measuring method used by the first non-subtlety fine particles of this invention is desirable, and the thing of 80-140m2/g within the limits is a thing of 90-130m2/g more preferably. Moreover, it is good the 0.05 - 1.5 weight section and that silica pulverized coal carries out 0-1.3 weight section use preferably to the magnetic toner 100 weight section.

[0051] As the magnetic substance used for the toner of this invention, there is a metallic oxide containing elements, such as iron, cobalt, nickel, copper, magnesium, manganese, aluminum, and silicon, etc. Especially, what uses iron oxides, such as a tri-iron tetraoxide and gamma-iron oxide, as a principal component is desirable. It is desirable to contain a silicon atom from a viewpoint of the fluid improvement in a toner and electrification nature control furthermore. If especially a toner particle becomes a minor diameter, since the fluidity of a toner particle parent will fall, the case where it is difficult not to acquire fluidity sufficient by just adding the non-subtlety fine particles of this invention mentioned above, but for it to become impossible to obtain good electrification nature, and to attain the purpose of this invention arises. It is desirable to contain 0.2 to 2.0% of the weight to the magnetic substance, when fewer than 0.2, sufficient fluidity is not acquired, but evils, such as aggravation of alphabetic character Sharp nature and solid \*\*\*\*\*, produce the content of a silicon atom. Especially if it is made to contain more mostly than 2.0, in an elevated temperature and a high-humidity environment, it will be easy to produce an image concentration fall. It is 0.3 - 1.7% of the weight of a case more preferably. The case where 0.05 - 0.5 % of the weight of silicon atoms exists on the surface of the magnetic substance especially is more desirable.

[0052] You may add to a magnetic-substance generate time in the form of a water-soluble silicon compound, it may add in the form of a silicic-acid compound after generation of the magnetic substance, filtration, and desiccation, and the surface may be made to fix a silicon atom by mix Mahler etc. The BET specific surface area by the nitrogen adsorption process is desirable, the particle of these magnetic substance has good 2-30m2/g, and its 3-28m2/g is especially good. Furthermore, the magnetic particle of 5-7 has desirable Mohs hardness.



[0053] As a configuration of a magnetic particle, although there is the shape of eight face pieces, six face pieces, a globular form, a needle, and a scale etc., what has the few anisotropy of eight face pieces, six face pieces, a globular form, an indeterminate mold, etc. is desirable. It is desirable when it raises image concentration especially that the degree of sphericity psi of a magnetic particle is 0.8 or more. As mean particle diameter of a magnetic particle, 0.05–1.0 micrometers is especially desirable still more desirable, and 0.1–0.4 micrometers is desirable 0.1–0.6 micrometers.

[0054] the content of the magnetic substance in a toner — the binding resin 100 weight section — receiving — the 30 – 200 weight section — the 60 – 200 weight section, and further 70 – the 150 weight sections are preferably good. Under in 30 weight sections, it was inferior in respect of conveyance nature, there was orientation which unevenness arises in the toner layer on developer support, and serves as image unevenness, and there was orientation which the fall of the image concentration which originates in the rise of TORIBO of a magnetic toner further tends to produce. On the other hand, when the content of the magnetic substance exceeded the 200 weight sections, the orientation which a problem produces was in fixable.

[0055] It is desirable to use an organometallic compound for the toner for electrostatic-charge image development of this invention as an electric charge control agent. What contains the organic compound which is rich in especially volatility and sublimability as a ligand or a counter ion also among organometallic compounds is useful.

[0056] There is an azo system metal complex expressed with the general formula [I] shown below as such a metal complex.

[0057]

[Formula 2]



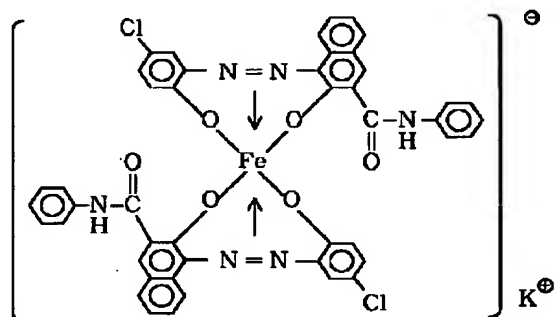
[0058] Among a formula, M expresses a coordination center metal and Cr, Co, nickel, Mn, Fe, aluminum, Ti, Sc, V, etc. of the coordination number 6 are raised. Ar is an aryl group, and a phenyl group, a naphthyl group, etc. are raised and it may have a substituent. As a substituent in this case, there are a nitro group, a halogen radical, a carboxyl group, an anilide radical and an alkyl group of carbon numbers 1–18, an alkoxy group, etc. X, X', Y, and Y' is –O–, –CO–, –NH–, and –NR– (R is the alkyl group of the charcoal <TXF FR=0002 HE=040 WI=080 LX=1100 LY=0600> prime factors 1–4). K<sup>+</sup> shows a hydrogen ion, sodium ion, potassium ion, ammonium ion, aliphatic series ammonium ion, or the mixed ion of one of these.

[0059] The example of the complex used for this invention good below is shown.

[0060]

[Formula 3]

式 (a)



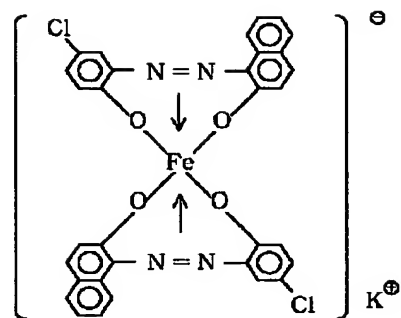
[K<sup>+</sup>: H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, 脂肪族アンモニウムイオン、あるいは

これらいずれかの混合イオンを示す。]

[0061]

[Formula 4]

式 (b)



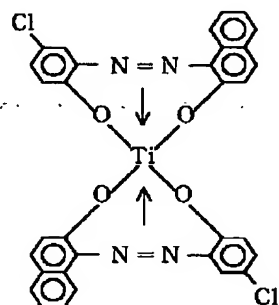
[ $K^{\oplus}$ :  $H^{\oplus}$ ,  $Na^{\oplus}$ ,  $K^{\oplus}$ ,  $NH_4^{\oplus}$ , 脂肪族アンモニウムイオン、あるいは

これらいずれかの混合イオンを示す。]

[0062]

[Formula 5]

式 (c)



[0063] As for this compound, it is desirable to be added in the range of 0.2 - 5 weight section to the toner 100 weight section.

[0064] As a class of binding resin used for this invention For example, the single polymer of styrene substitution products, such as polystyrene; Polly p-KURORU styrene and polyvinyl toluene; A styrene-p-KURORU styrene copolymer, A styrene-vinyltoluene copolymer, a styrene-vinyl naphthalene copolymer, A styrene-acrylic ester copolymer, a styrene-methacrylic ester copolymer, A styrene-alpha-Krol methyl-methacrylate copolymer, a styrene-acrylonitrile copolymer, A styrene-vinyl methyl ether copolymer, a styrene-vinyl ethyl ether copolymer, A styrene-vinyl methyl ketone copolymer, a styrene-butadiene copolymer, Styrene system copolymers, such as a styrene-isoprene copolymer and a styrene-acrylonitrile-indene copolymer; A polyvinyl chloride, Phenol resin, natural denaturation phenol resin, natural resin denaturation maleic resin, Acrylic resin, methacrylic resin, Pori acetic-acid vinyl, silicone resin, polyester resin, polyurethane, polyamide resin, furan resin, an epoxy resin, xylene resin, a polyvinyl butyral, terpene resin, cumarone indene resin, petroleum system resin, etc. can be used. Moreover, the styrene resin over which the bridge was constructed is also desirable binding resin.

[0065] As a comonomer to the styrene monomer of a styrene system copolymer For example, an acrylic acid, a methyl acrylate, an ethyl acrylate, butyl acrylate, Acrylic-acid dodecyl, acrylic-acid octyl, 2-ethylhexyl acrylate, Acrylic-acid phenyl, a methacrylic acid, a methyl methacrylate, ethyl methacrylate, The monocarboxylic acid which has double bonds, such as methacrylic-acid butyl, methacrylic-acid octyl, acrylonitrile, a methacrylonitrile, and acrylamide, or its substitution product; for example The dicarboxylic acid which has double bonds [ like ], such as a maleic acid, maleic-acid butyl, maleic-acid methyl, and maleic-acid dimethyl, and its substitution product; for example Ethylene system olefins, such as vinyl ester, for example, ethylene, such as a vinyl chloride, vinyl acetate, and benzoic-acid vinyl, a propylene, and a butylene; for example vinyl monomers, such as vinyl ether [ , such as vinyl ketones /, such as a vinyl methyl ketone and a vinyl hexyl ketone, /, for example vinyl methyl ether, vinyl ethyl ether, and the vinyl isobutyl ether, ], are independent — or it is combined and used. Carboxylate which the compound which mainly has the double bond in which two or more polymerizations are possible as a cross linking agent here is used, for example, has two double bonds, such as aromatic series divinyl compound [ , such as a divinylbenzene and divinyl naphthalene, ], for example, ethylene glycol diacrylate, ethylene glycol dimethacrylate, and 1,3-butanediol dimethacrylate; compound; which has divinyl compound [ , such as a divinyl aniline, the divinyl ether, a divinyl sulfide, and a divinyl sulfone, ]; and three or more vinyl groups can use it as independent or mixture.

[0066] Moreover, as binding resin of the toner with which pressure fixing is presented, low molecular weight polyethylene, low molecular weight polypropylene, an ethylene-vinylacetate copolymer, an ethylene-acrylic ester copolymer, a higher fatty acid, polyamide resin, and polyester resin are mentioned. As for these, independent or mixing and using are desirable.

[0067] Moreover, it is desirable to also make the following waxes contain in a toner particle from the point of improvement in the mold-release characteristic from the fixing member at the time of fixing and improvement in fixable. An oxide, and a block copolymer with a vinyl system monomer and a graft denaturation object are included in

a derivative with paraffin wax and its derivative, a micro crystallin wax and its derivative, the Fischer Tropsch wax and its derivative, a polyolefine wax and its derivative, carnauba wax, its derivative, etc.

[0068] As other additives, alcohol, a fatty acid, an acid amide, ester, a ketone, hydrogenated castor oil and its derivative, a vegetable system wax, an animal wax, a mineral system wax, a PETORO lactam, etc. can be used.

[0069] In order to produce the toner of this invention, a well-known method is used. For example, binding resin, a wax, a metal salt or a metal complex, the pigment as a coloring agent, A color or the magnetic substance, and necessity are accepted. An electric charge control agent, other additives, etc. A Henschel mixer, After mixing enough with mixers, such as a ball mill, a heating roller, a kneader, Metallic compounds, a pigment, a color, and the magnetic substance are made to be able to distribute or dissolve in the inside in which carried out melting kneading using the heat kneading machine like an extruder, and each was made to dissolve resin, and the toner which performs grinding and a classification and is applied to this invention can be obtained after cooling solidification. It is desirable to use a hyperfractionation classifier on productive efficiency in a classification production process.

[0070] An example of image formation equipment is roughly shown in drawing 2, and the image formation method is explained based on it.

[0071] 1 is electrostatic rotating-drum-like latent-image support, and the developer 4 which has primary electrification equipment 2, the exposure optical system 3, and the toner support 5, imprint equipment 9, and cleaning equipment 11 are arranged in the perimeter.

[0072] In this image formation equipment, the surface of the electrostatic latent-image support 1 which is a photo conductor is uniformly charged with primary electrification equipment 2, image exposure is carried out according to the exposure optical system 23, and an electrostatic latent image is formed in the surface of the electrostatic latent-image support 1.

[0073] Subsequently, on the surface of the toner support 5 which connects a magnet, the electrostatic latent image formed at the electrostatic latent-image support 1 is developed by the toner thickness specification-part material 6, forming a toner coat layer based on the configuration of this invention, and impressing mutual bias, pulse bias, and/or direct-current bias in the development section with the bias impression means 8 between the conductive base of the electrostatic latent-image support 1, and the toner support 5.

[0074] The developed toner image conveys a transfer paper P, with imprint equipment 9 and the voltage impression means 10, it adds a toner and the charge of reversed polarity from the back of a transfer paper P, and electrostatic image transfer is carried out to a transfer paper P.

[0075] In the transfer paper P which imprinted the toner, a fixing image is obtained by passing the heating pressurization roller fixing assembly 12.

[0076] The toner which remains on the latent-image support after an imprint production process is removed by cleaning equipment 11, and the production process below primary electrification is repeated again.

[0077]

[Example] The concrete example of this invention is shown below. The "section" means the weight section.

[0078] Example 1 Binding resin The 100 sections Magnetic substance (Fe 3O4 of 0.12 % of the weight of silicon atom contents) The 100 sections Monoazo color metal complex (formula a) The two sections Wax The five sections

[0079] Mixed distribution of the above-mentioned component was carried out with the Henschel mixer, and melting kneading was performed by the 2 shaft extruder. After cooling, coarse grinding of the kneading object was carried out, it was pulverized with the grinder using a jet stream, classified using the pneumatic elutriation machine further, and obtained the toner particle.

[0080] pH=5.9, bulk density which carried out coupling processing of the original object silica (specific-surface-area =300m2/g) 100 section in the hexamethyldisilazane 10 section to this toner particle 100 section = the non- [ 72g /l. ] subtlety fine particles L-1 (specific-surface-area =197m2/g) were mixed with 1.2 \*\*\*\*\* and a Henschel mixer, and the weight mean diameter X= 7.2 (micrometer) and the toner for electrostatic-charge image development of Y= 5.0 (%) were obtained.

[0081] The obtained toner was thrown into printer LJ-IV made from HP, and it evaluated according to the following image evaluation methods.

[0082]

(Example of manufacture of toner support)

Graphite (4 micrometers of diameters of a major axis) The 100 sections Resol mold phenol resin The 200 sections Methanol The 130 sections Isobutyl alcohol The 160 sections [0083] The above-mentioned component was distributed in the sand mill for 2 hours using the media particle which consists of zirconia beads with a diameter of 1mm, the bead was separated using the sieve, and the undiluted solution for covering was obtained. Furthermore, diluted this undiluted solution with isopropyl alcohol to 25% of solid content, considered as coating liquid, applied on the support base made from stainless steel with a diameter of 20mm with the spray method, made covering with a thickness of 9 micrometers form, and continued, and heat 150 degrees C for 30 minutes at a hot-air-drying furnace, it was made to harden, and the toner support of Ra=0.8 was produced.

[0084] Thus, the elastic blade made from urethane was made to contact the produced toner support, and the toner layer was regulated. In addition, the amount of coats per unit area of the toner thin layer on the toner support in the first stage is 1.1 mg/cm2, and w/rho at that time was set as 0.64.

[0085] Evaluation of image nature checked in the durability (about 5000 sheets) of LJ-IV, and evaluated in ordinary temperature and normal-relative-humidity environment (23.5 degrees C, 60%) periodically.

[0086] - Alphabetic character Sharp nature -- Using the 1000-sheet o'clock check sample, the alphabetic character

of “\*\*” of about 2mm angle was expanded by about 30 times, and it evaluated in accordance with the following error criteria.

[0087]

O (A) : Rhine is very sharp and there is almost no spilling.

O (Good) : Rhine is Sharp comparatively at the degree which has scattered slightly.

\*\* (usually): Spilling becomes the sensibility which Rhine carried out vacantly a little mostly.

x(bad): Don't fulfill the level of \*\*.

[0088] - Solid black concentration — To the initial -5000 sheet, a total of 26 samples in every 200 sheets were measured from the Macbeth concentration meter, and it was shown with the average.

[0089] - Fogging — The value of one point from which the whiteness degree of the transfer paper before a print is beforehand measured, and a difference with the whiteness degree of the printed whole surface white image serves as max was measured using “RIFUREKUKU meter” (Tokyo Denshoku Co., Ltd. make), and the greatest value was shown through durability (about 5000 sheets).

[0090] - Escape among an alphabetic character. — The pasteboard of 128g/m<sup>2</sup> was made to print a general alphabetic character, and the average of six samples of 1000 sheets, 2000 sheets, 3000 sheets, 4000 sheets, and 5000 sheets estimated the first stage. rank 5: — fitness (refer to (a) of drawing 1), and rank 1: — practically improper (refer to (b) of drawing 1), and rank 3: — good and ranks 4 and 2 are practically taken as the middle level of ranks 5 and 3 and ranks 3 and 1, respectively.

[0091] - Drum welding — It evaluated from the generating condition of white Poti of the solid black image after durable termination.

[0092] O O: of which :generating is not done — it generates slightly — do \*\*:generating of.

[0093] The same method as an example 1 estimated except changing example 2 toner particle size. A result is shown in a table 1.

[0094] The same method as an example 1 estimated except using the toner which added M-1 [ 0.1-section ] [what [ processed the silica pulverized coal (110m<sup>2</sup>/g) 40 section compounded with the wet method in the dimethyl silicone oil (12500cSt) 60 section ], bulk density 0.4g/cm<sup>3</sup>, and specific-surface-area 3.0m<sup>2</sup>/g] as the second example 3 inorganic pulverized coal. A result is shown in a table 1.

[0095] The 0.8 sections and M-1 to a 0.1 section pan for L-1 as example 4 inorganic pulverized coal as the third inorganic pulverized coal N-1 [what [ processed the pulverized coal 100 section which carried out coupling processing of the original object silica (specific-surface-area 200m<sup>2</sup>/g) 100 section and the hexamethyldisilazane 10 section by dimethyl silicone oil (100cSt) ], 45g [/. ] bulk density, and specific-surface-area 120m<sup>2</sup>/g] The same method as an example 1 estimated except using the toner which carried out 0.7 section addition. A result is shown in a table 1.

[0096] The same method as an example 1 estimated except making it development conditions as show the aluminum element tube surface in a table 1 as example 5 toner support using what processed the mirror plane (Ra=0.3). A result is shown in a table 1.

[0097] The same method as an example 5 estimated except adding the 0.1 sections of third non-subtlety fine particles M-1 to example 6 toner. A result is shown in a table 1.

[0098] The same method as an example 5 estimated except using for example 7 toner the toner which added three sorts of non-subtlety fine particles like the example 4. A result is shown in a table 1.

[0099] As the first example 8 inorganic pulverized coal, the toner (X= 5.8 micrometers, Y= 17.5%) was obtained by the same method as an example 1 except adding L-2 [ 1.5-section ] (pH=6.3, bulk density = 165g/(l.)). The same method as an example 1 estimated below. A result is shown in a table 1.

[0100] The same method as an example 1 estimated except using the toner support of Ra=1.5 produced by the same method as an example 1 except adding further the PMMA particle (number pitch diameter of 6.5 micrometers) 15 section as example 9 toner support. However, the toner used X= 5.8 micrometers and Y= 17.5% of thing. The same method as an example 1 estimated below. A result is shown in a table 1.

[0101] The toner (X= 5.3 micrometers, Y= 23%) was obtained by the same method as example 10 example 1. The same method as an example 1 estimated below. A result is shown in a table 1.

[0102] As example of comparison 1 toner support, the coat sleeve of Ra=2.5 produced by the same method as an example 1 was used except adding further the PMMA particle (number pitch diameter of 6.5 micrometers) 25 section. As the first inorganic pulverized coal, L-4 [ 1.0-section ] [pH=3.0 and bulk density =35g/(l.)] was added, and toner grain size used X= 7.8 micrometers and Y= 4.0% of thing. About the process and appraisal method of a toner, it carried out by the same method as an example 1. A result is shown in a table 1.

[0103] As example of comparison 2 toner support, what was used in the example 5, and the same thing were used. Adding L-4 [ 1.2-section ] as non-subtlety fine particles, toner grain size used X= 5.1 micrometers and Y= 31.0% of thing. About the process and appraisal method of a toner, it carried out by the same method as an example 1. A result is shown in a table 1.

[0104]

[A table 1]

	スリープ Ra	W (mg/cm <sup>2</sup> )	$\rho$ (g/cm <sup>3</sup> )	w/ $\rho$	無機微粉体			粒 度		画 質				耐ドラム 融 着
					第一	第二	第三	D <sub>1</sub> ( $\mu$ m)	3.17 $\mu$ m 以下(%)	文 字 シャープ性	ベタ黒 濃 度	カブリ	中抜け	
実施例 1	0.8	1.1	1.73	0.64	L-1	-	-	7.2	5.0	○ <sup>△</sup>	1.45	1.8	3	△
2	0.8	0.9	1.72	0.52	L-1	-	-	5.8	17.5	○	1.42	2.2	3	△
3	0.8	0.9	1.72	0.52	L-1	M-1	-	5.8	17.5	○	1.40	2.5	4	○
4	0.8	0.9	1.72	0.52	L-1	M-1	N-1	5.8	17.5	○	1.40	2.3	5	◎
5	0.3	0.6	1.72	0.35	L-1	-	-	5.8	17.5	◎	1.37	2.9	3	△
6	0.3	0.6	1.72	0.35	L-1	M-1	-	5.8	17.5	◎	1.37	2.6	4	○
7	0.3	0.6	1.72	0.35	L-1	M-1	N-1	5.8	17.5	◎	1.37	2.4	5	◎
8	0.8	0.9	1.72	0.52	L-2	-	-	5.8	17.5	○ <sup>△</sup>	1.30	2.7	3	△
9	1.6	1.2	1.72	0.70	L-1	-	-	5.8	17.5	○ <sup>△</sup>	1.42	1.7	3	△
10	0.8	0.8	1.72	0.46	L-1	-	-	5.5	26.0	○	1.37	3.0	3	△
比較例 1	2.5	1.6	1.72	0.93	L-4	-	-	7.8	4.0	×	1.30	2.0	2	△
2	0.3	0.3	1.72	0.17	L-4	-	-	5.1	31.0	△	1.20	4.3	2	△

[0105]

[Effect of the Invention] The fluidity of this invention of a toner improved by adding specific non-subtlety fine particles, it became possible to make electrification nature [ still fitness / a toner ] give of it, especially in the thin layer coat system, alphabetic character Sharp nature was good, solid black concentration was high, generating of fogging was controlled, and it became possible [ forming an image with the still better omission in an alphabetic character ].

[Translation done.]

**\* NOTICES \***

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown typically the good example (a) of an imprint condition, and the poor example (b) of an imprint condition in the general alphabetic character.

[Drawing 2] It is drawing having shown the outline of an example of the image formation equipment used for the image formation method of this invention.

[Description of Notations]

- 1 Latent-Image Support
- 2 Primary Electrification Equipment
- 3 Exposure Optical System
- 4 Developer
- 5 Toner Support
- 6 Toner Thickness Specification-Part Material
- 7 Toner Churning Means
- 8 Development Bias Power Supply
- 9 Imprint Equipment
- 10 Imprint Current Generator
- 11 Cleaning Means
- 12 Anchorage Device
- 13 Magnetic Toner

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[Translation done.]

## \* NOTICES \*

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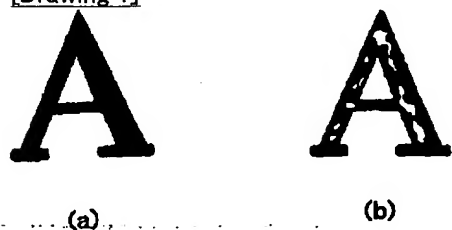
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
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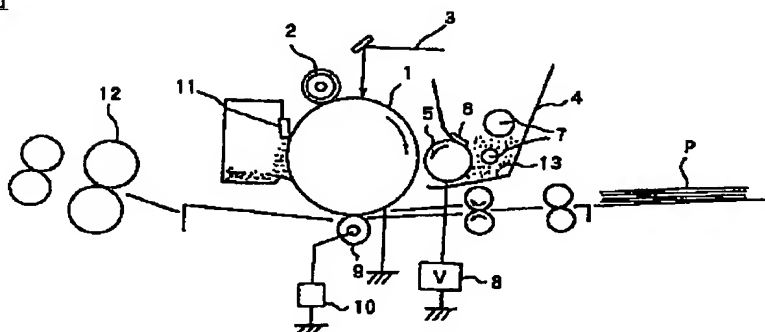
DRAWINGS

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[Drawing 1]



[Drawing 2]




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[Translation done.]

特開平9-62030

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9/083			15/08	504Z
9/097				507L
15/08	504		9/08	
	507			101
審査請求 未請求 請求項の数10 FD (全12頁) 最終頁に続く				
(21)出願番号	特開平7-23061	(71)出願人	000001007	
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## (54)【発明の名称】 画像形成方法

## (57)【要約】

【課題】 シャープな文字を形成し、ベタ黒濃度が良好でかつカブリの少ない画像を形成することが可能な画像形成方法を提供することにある。

【解決手段】 静電潜像担持体と対向したトナー担持体上にトナー層を形成して、静電潜像担持体上の静電潜像を現像する工程を有する画像形成方法において、トナー担持体上に形成されるトナー層の単位面積当たりのコー

ト量が、

$$w/\rho = 0.2 \sim 0.8$$

w: トナー担持体表面1cm<sup>2</sup>あたりのトナーコート重量 (mg)

$\rho$ : トナー真密度 (g/cm<sup>3</sup>)

を満たすように設定され、該トナー担持体表面の平均粗度Raが1.8以下であり、該トナーは少なくともトナー粒子及び無機微粉体を有し、該無機微粉体が、シリカカップリング剤で処理され、濃度が6.0~18.0g/リットルでpHが4.5~8.5であることを特徴とする画像形成方法に関する。

(2)

1

## 【特許請求の範囲】

【請求項1】 静電潜像担持体と対向したトナー担持体上にトナー層を形成して、静電潜像担持体上の静電潜像を現像する工程を有する画像形成方法において、トナー担持体上に形成されるトナー層の単位面積当たりのコート量が、

$$w/\rho = 0.2 \sim 0.8$$

w: トナー担持体表面1cm<sup>2</sup>あたりのトナーコート重量 (mg)

$\rho$ : トナー真密度 (g/cm<sup>3</sup>)

を満たすように設定され、該トナー担持体表面の平均粗度Raが1.8以下であり、

該トナーは少なくともトナー粒子及び無機微粉体を有し、該無機微粉体が、シリカカップリング剤で処理され、濃度が6.0~18.0g/リットルでpHが4.5~8.5であることを特徴とする画像形成方法。

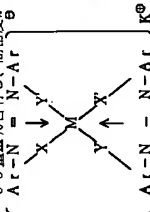
【請求項2】 該トナーの粒度分布が、重量平均径(D<sub>4</sub>)をX(μm)、個数分布から求めた個数基準の3.17μm以下の個数%をY(%)とした時、下記条件-5X+3.5≤Y≤-2.5X+18.0

$$3.5 \leq X \leq 6.5$$

を満たすことを特徴とする請求項1に記載の画像形成方法。

【請求項3】 該トナー粒子100重量部に対して、該無機微粉体が0.05~3重量部添加されていることを特徴とする請求項1又は2に記載の画像形成方法。

【請求項4】 該トナー中に、シリコンオイルまたはシリコンワックスを20~90重量%含有し、濃度が\*



あるいは



[M: Fe, Mn, Al, Ni, Co, Cr, Sc, Ti, V]

Ar: フェニル基、ナフチル基、

置換基 (ニトロ基、ハロゲン基、カルボキシル基、アニリド基、

炭素数1~18のアシル基あるいはアルコキシ基) を有する

フェニル基あるいはナフチル基を示す。

X, X', Y, Y': -O-, -NH-, -NR- (Rは炭素数1~4の

アルキル基) を示す。

K<sup>⊕</sup>: H<sup>⊕</sup>, Na<sup>⊕</sup>, K<sup>⊕</sup>, NH<sub>4</sub><sup>⊕</sup>, 脂族アンモニウムイオン、あるいは

これらいずれかの複合イオンを示す。】

【発明の詳細な説明】

[0001]

【発明の属する技術分野】 本発明は、電子写真法、静電50 記録法の如き画像形成方法に関するものである。

特開平9-62030

2

\*0.2~0.8g/m<sup>2</sup>で比表面積が0.01~50m<sup>2</sup>/gである第二の無機微粉体を含有することを特徴とする請求項1乃至3のいずれかに記載の画像形成方法。

【請求項5】 該トナー粒子100重量部に対して、第二の無機微粉体が0.02~1重量部添加されていることを特徴とする請求項4に記載の画像形成方法。

【請求項6】 該トナー中に、シリカカップリング剤処理後、シリコンオイルまたはシリコンワックスにより処理された濃度が3.0~6.0g/リットルで比表面積が8.0~14.0m<sup>2</sup>/gである第三の無機微粉体を含有することを特徴とする請求項1乃至5のいずれかに記載の画像形成方法。

【請求項7】 該トナー粒子100重量部に対して、第三の無機微粉体が0.05~3重量部添加されていることを特徴とする請求項6に記載の画像形成方法。

【請求項8】 該トナー粒子中に、磁性体を含有し、ケイ素原子が該磁性体に対して0.2~2.0重量%含有されていることを特徴とする請求項1乃至7のいずれかに記載の画像形成方法。

【請求項9】 該トナー粒子が少なくとも結着樹脂及び磁性体を含有し、該結着樹脂100重量部に対して、該磁性体が7.0~15.0重量部含有されていることを特徴とする請求項8に記載の画像形成方法。

【請求項10】 該トナー粒子中に、荷電制御剤として下記式で示される有機金属化合物を含有していることを特徴とする請求項1乃至9のいずれかに記載の画像形成方法。





【0002】従来の技術 従来、電子写真法としては多数の方法が知られている。一般には光導電性物質を利用して、種々の手段により像担持体（感光体）上に電気的潜像を形成し、次の露光像をトナーで現像を行なって可視像とし、必要に応じて紙などの転写材にトナー像を転写した後、熱・圧力等により転写材上にトナー画像を定着して複写物を得るものである。

【0003】近年、電子写真法を用いた機器は、従来の複写機以外にプリンターやファクシミリ等多数になってきている。

【0004】たとえば、プリンター装置はLEDまたはLBPプリンターが最近の市場の主流になっており、技術の方向としてより高解像度即ち、従来240・300dpiであったものが400・600・800dpiとになってきている。従って現像方式もこれにともなってより高解像度が要求されてきている。また、複写機においても高解像度が進んでおり、そのためデジタル化の方向に進みつつある。この方向は、静電荷像をレーザで形成する方法が主であるが、やはり高解像度の方向に進んでおり、ここでもプリンターと同様に高解像・高解像の現像方式が要求されてきている。このためトナーの小粒化が進んでおり、特開平1-112253号公報、特開平1-191156号公報、特開平2-214156号公報、特開平2-284158号公報、特開平3-181952号公報、特開平4-162048号公報などで特定の粒度分布の粒径の小さいトナーが提案されている。

【0005】一方、現像方式としては、プリンターやファクシミリ等の小型化、軽量化の観点から、一成分現像方式が好ましく用いられている。その中でもトナー担持体と静電潜像担持体とをある一定の間隔において配置し、トナー担持体上に潜像担持体と接触しないトナー層を形成して、さらにトナー担持体と潜像担持体間に交互電界を印加して現像を行なう、ジャンピング現像方式（特昭58-32375号公報等）が好ましく用いられている。

【0006】しかし、この現像方法においても、さらなる高解像度画像を形成する為に、静電潜像担持体上の潜像により忠実にトナーを現像させる方法が検討されている。たとえば露出面積当りの重量を減じない方向は、画質の高解像化の方向に好適に用いられる方法であるが、上述の小粒化トナーを用いた場合にベタ黒濃度及びカバリの発生がみられ、満足する画像が得られないのが現状である。

【0007】従来以上の高解像度画像が達成でき、ベタ黒濃度が高くかつカバリの少ない画像を形成可能な画像形成方法を提供するには、トナーとして基本的に流動性の向上が望まれている。

【0008】トナーの流動性を確保する一手段として、

特開平5-66608号公報、特開平4-98660号公報等で疎水化処理を施した無機微粉体若しくは疎水化処理した後さらにシリコーンオイル等で処理した無機微粉体を追加、あるいは特開昭61-249059号公報、特開平4-266453号公報、特開平5-346682号公報で疎水化処理無機微粉体とシリコーンオイル処理無機微粉体を併用添加する方法が知られている。

【0009】しかし、これらの手法を用いたトナーを用いても、依然として文字シャープ性、ベタ黒濃度及びカバリのパラメータを保持することは困難な状況にあった。

【0010】

【発明が解決しようとする課題】本発明の目的は、シャープな文字を形成し、ベタ黒濃度が良好でかつカバリの少ない画像を形成することが可能な画像形成方法を提供することにある。

【0011】また、本発明の目的は、上記の目的を達成し、かつ中抜けのない文字を形成することが可能な画像形成方法を提供することにある。

【0012】

【課題を解決するための手段及び作用】本発明は、下記構成によって前記の目的を達成する。

【0013】すなわち、本発明は、静電潜像担持体と対向したトナー担持体上にトナー層を形成して、静電潜像担持体上の静電潜像を現像する工程を有する画像形成方法において、トナー担持体上に形成されるトナー層の厚さを、 $w/\rho = 0.2 \sim 0.8$

$w$ ：トナー担持体表面1cm<sup>2</sup>あたりのトナーコート重量（mg）  
 $\rho$ ：トナー真密度（g/cm<sup>3</sup>）  
を満たすように設定され、該トナー担持体表面の平均粗度Raが1・8以下であり、該トナーは少なくともトナー粒子及び無機微粉体を有し、該無機微粉体が、シランカップリング剤で処理され、濃度が60～180g/リットルでpHが4・5～8・5であることを特徴とする画像形成方法に関する。

【0014】現像方法に関しては、 $w/\rho$ が0・2より小さい場合はベタ黒濃度が十分確保されず好ましくない。w/ρが0・8より大きい場合は、文字周辺部に飛び散りが増大し、シャープな文字が形成されず好ましくない。またトナー担持体の平均表面粗度Raが1・8より大きい場合は、シャープな文字が形成されず好ましくない。より好ましくはRaが1・5以下の場合である。それゆえに、本発明の様な現像条件を有することが本発明の目的を達成するのに必要となる。

【0015】さらにこの様な現像条件に対して、シランカップリング剤で処理され、濃度が60～180g/リットルで、かつpHが4・5～8・5であることを特徴とする無機微粉体を含有するトナーを組み合わせたことが必要である。

【0016】該無機微粉体の濃度が60g/リットルより小さい場合は、トナーに十分な流動性を付与することができ、本発明の様なトナー層を薄層にする系においては、均一なトナーコート層が形成されず、十分なベタ黒濃度が得られない。濃度が180g/リットルより大きい場合と同様にトナーの流動性の低下が生じ、本発明の様な薄層系においては、均一なトナーコート層が形成されず、十分なベタ黒濃度が得られない。

【0017】さらに、この時添加する無機微粉体のpH値が中性域のものが文字のシャープ性、画像濃度及び文字中抜けにおいて良好な傾向を有する。トナー粒子は、一般的に、荷電制御剤あるいは結着樹脂等で負か正の一方の荷電性を有する構成剤とする。この荷電方向に対してトナーの荷電性を適度に増大させたり減じさせる様な電荷を付与させる無機微粉体を添加することは、そのメカニズムは明確ではないが、特に本発明で用いられる様な薄層コート系の現象方式においては弊害が生じ易い。たとえば負荷電性トナーの場合、pHが4・5より小さいと飛び散りの悪化が見られ文字のシャープ性が低下する。8・5より大きいとベタ黒濃度の低下、文字中抜けの悪化傾向がみられる。より好ましく用いられる範囲は5・0～8・0である。

【0018】なお、本発明のトナー真密度は高品質製作所製の顕微鏡自動密度計「アキュビック1330」により測定したデータを用いた。

【0019】中心線平均粗さ（Ra）は、JIS表面粗さ（BO601）に基づいて、表面粗さ測定器（サーフコーダSE-30H、株式会社小坂研究所）を用いて測定される。具体的には、中心線粗さ（Ra）は、粗さ曲線からその中心線方向に測定長さa2・5mmの部分抜き取り、この抜き取り部分の中心線をX軸、縦断面の方向をY軸、粗さ曲線をy=f(x)で表わした時、次の式によって求められる値をミクロメートル（μm）で表わしたものをいう。

【0020】

【数1】

$$Ra = \frac{1}{a} \int_0^a |f(x)| dx$$

【0021】本発明に用いられるトナー担持体としては、たとえばステンレス、アルミニウム等から成る円筒状、あるいはペレット状部材が好ましく用いられる。また、必要に応じて表面を金属、樹脂等のコートしても良く、樹脂や金属類、カーボンブラック、荷電制御剤等の微粒子を分散した樹脂をコートしても良い。

【0022】

【発明の実施の形態】本発明で用いられる無機微粉体としては、シリカ、アルミナ、チタニアなどが使用でき、特にシランカップリング剤処理前の原形シリカはケイ酸微粉体が良好に使用される。

【0023】ケイ酸微粉体はケイ酸ハロゲン化合物の蒸気

相酸化により生成されたいわゆる乾式法又はヒュームドシリカと称される乾式シリカ、及び水ガラス等から製造されるいわゆる湿式シリカの両者が使用可能であるが、表面及びシリカ微粉体の内部にあるシランノール基が少なく、またNa<sub>2</sub>O、SO<sub>3</sub>等の製造残滓の少ない乾式シリカの方が好ましい。また乾式シリカにおいては、製造工程において例えば、塩化アルミニウム、塩化チタン等の他の金属ハロゲン化合物をケイ酸ハロゲン化合物と共に用いることによって、シリカと他の金属酸化物の複合微粉体を得ることも可能でありそれらも包含する。

【0024】シランカップリング剤としては、例えばヘキサメチルジシラザン、トリメチルシラン、トリメチルクロルシラン、トリメチルエトキシシラン、ジメチルクロルシラン、メチルトリクロルシラン、アリルジメチルクロルシラン、アリルフエニルジクロルシラン、ベンジルジメチルクロルシラン、ブロメチルジメチルクロルシラン、α-クロルエチルトリクロルシラン、β-クロルエチルトリクロルシラン、クロメチルジメチルクロルシラン、トリオクタシルメチルメチルアブタン、トリメチルシランメチルアブタン、トリオクタシルシリルアクリレート、ビニルジメチルアセトキシシラン、ジメチルジエトキシシラン、ジメチルセトキシシラン、ジフェニルジエトキシシラン、ヘキサメチルジシロキサン、1・3ジエトキシシラン、ニルデトラメチルジシロキサン、1・3-ジフェニルデトラメチルジシロキサン及び1分子当たり2から12個のシロキサン単位を有し末端に位置する単位にそれぞれ1個位のケイ基原子に結合した水酸基を含有したジメチルシロキサン等が挙げられる。

【0025】上記微粉体のシランカップリング剤処理は、微粉体を溶剤等によりクラウド状としたものに酸化したシランカップリング剤を反応させる乾式処理、又は、微粉体を溶剤中に分散させシランカップリング剤を滴下反応させる湿式法等の方法で処理することができ、中でも特に乾式処理法が好ましく用いられるがこれに限定されるものではない。

【0026】濃度を高める方法としては、ケイ酸微粉体をケイ酸ハロゲン化合物を生成する際の反応条件によって、あるいはシランカップリング剤処理する前もしくは後に機械的（ヘンシェルミキサー、ミックスマラー等）な作用により粒子同士を凝集させる方法が挙げられる。

【0027】本発明で用いられる無機微粉体はBET法で測定した蒸気吸着による比表面積が100m<sup>2</sup>/g以上、特に150～400m<sup>2</sup>/gの範囲のものが好ましい。

【0028】また、本発明の無機微粉体はトナー粒子100重量部に対して0・05～3重量部添加することが好ましい。

【0029】本発明においてpH測定はガラス電極を用いたpHメーターを用いて行う。試料4gをピーカーに





【0074】現像したトナー像は、転写紙Pを搬送し転写装置9、電圧印加手段10により、転写紙Pの背面からトナーと逆極性の電荷を加えて、転写紙Pへ静電転写される。

【0075】トナーを転写した転写紙Pを、加熱加圧ローラ定着器12を通過させることにより定着画像が得られる。

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#### 結着剤指

磁性体 (ケイ素原子含有量0.12重量%の $\text{Fe}_3\text{O}_4$ )  
モノアノ染料系金属結晶 (式a)

#### フックス

【0079】上記構成材料をベンジエルミキサーで混合分散し、二軸エクストルuderで溶融混練を行なった。混練物は冷却後、粗粉砕し、ジェット気流を用いた粉砕機によって微粉砕し、更に風力分級機を用いて分級しトナー粒子を得た。

【0080】該トナー粒子100部に対して、原体シリカ (比較面積 $=300\text{m}^2/\text{g}$ ) 100部をヘキサメチルジシラン10部でカップリング処理した $\text{pH}=5$ 、※ (トナー担持体の製造例)。

グラファイト (長軸径 $4\mu\text{m}$ )

レゾール型フエノール樹脂

#### メタノール

#### インジカルアルコール

【0083】上記成分を直径1mmのジルコニアビーズからなるメデア粒子を用いてサンディルにて2時間分散し、フルイを用いてビーズを分離し、破棄用原液を得た。更に、この原液をインゾビアルアルコールで固形分25%に希釈して塗工液とし、スプレー法により直径20mmのステンレス製担持体基体上に塗布して厚さ $5\mu\text{m}$ の破覆を形成させ、続いて熱風乾燥炉により150℃、30分間加熱して硬化させ $\text{Ra}=0.8$ のトナー担持体を作製した。

【0084】この様に作製されたトナー担持体にクレタ製の弾性ブレードを当接させてトナー層を規制した。なお、初期におけるトナー担持体上のトナー層の単位面積当りのコート量は $1.1\text{mg}/\text{cm}^2$ で、そのときの $w/\phi$ は0.64に設定した。

【0085】画像性の評価は、常温・常照環境 (23.5℃、60%) でL-I-Vの苗久 (約5000枚) の中でチェックを定期的に実施し評価を行なった。【0086】・文字シャープ性…100枚時のチェックサンプルを用いて、約2mm角の「電」の文字を約30倍に拡大し、以下の評価基準に従い評価を行なった。

【0087】

◎ (像) : ラインが非常にシャープで飛び散りはほとんどない。

○ (点) : わずかに飛び散っている程度でラインは比較的にシャープ。

△ (普通) : 飛び散りがやや多くラインがぼんやりした

＊【0076】転写工程後の消像担持体上に残留するトナーは、クリーニング装置11により除去され、再び一次帯電以下の工程が繰り返される。

【0077】

【実施例】以下に本発明の具体的な実施例を示す。「部」は重量部を意味する。

【0078】実施例1

100部

100部

2部

5部

※9、濃密度 $=72\text{g}/\text{リットル}$ の無機微粉体L-1 (比較面積 $=197\text{m}^2/\text{g}$ ) を1.2部添加、ベンジエルミキサーで混合し、重量平均径 $X=7.2(\mu\text{m})$ 、 $Y=5.0(\%)$ の静電荷電処理用トナーを得た。

【0081】得られたトナーをHPP社製プリンターL-J-I-Vに投入し、以下の画像評価方法に従い評価を行なった。

【0082】

100部

200部

130部

160部

感じになる。

X (悪い) :  $\Delta$ のレベルに達しない。

【0088】・ベタ黒濃度…初期…5000枚まで200枚毎の計26サンプルをマックベス濃度計より測定しその平均値をもって示した。

【0089】・カブリ…“リフレクメーター” (東京電色 (株) 製) を用い、あらかじめプリント前の転写紙の白色度を測定し、プリントされた全面白画像の白色度との差が最大となる1点の値を測定し、苗久 (約5000枚) を通して最大の値を示した。

【0090】・文字中抜け… $128\text{g}/\text{m}^2$ の厚紙に一般文字を印字させて初期、1000枚、2000枚、3000枚、4000枚、5000枚の6サンプルの平均で評価した。ランク5 : 良好 (図1の(a)参照)、ランク1 : 実用上不可 (図1の(b)参照)、ランク3 : 実用上可、ランク4、2はそれぞれランク5と3、ランク3と1の中間レベルとする。

【0091】・ドラム融着…苗久終了後のベタ黒画像の白ボチの発生状況から評価した。

【0092】◎ : 発生しない、○ : わずかに発生する、△ : 発生する。

【0093】実施例2

トナー粒径を変える以外は、実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0094】実施例3

※ 第二無機微粉体としてM-1 [随式で合成されたシリ

カ微粉体 ( $110\text{m}^2/\text{g}$ ) 40部をジメチルシリコンオイル ( $1250\text{cSt}$ ) 60部で処理したものを、濃密度 $0.4\text{g}/\text{cm}^3$ 、比較面積 $3.0\text{m}^2/\text{g}$ を0.1部添加したトナーを用いる以外は実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0095】実施例4

無機微粉体としてL-1を0.8部、M-1を0.1部、さらに第二無機微粉体としてN-1 [原体シリカ (比較面積 $200\text{m}^2/\text{g}$ ) 100部とヘキサメチルジシラン10部をカップリング処理した微粉体100部をジメチルシリコンオイル ( $100\text{cSt}$ ) で処理したもの、濃密度 $45\text{g}/\text{リットル}$ 、比較面積 $120\text{m}^2/\text{g}$ ] を0.7部添加したトナーを用いる以外は実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0096】実施例5

トナー担持体として、アルミ素管表面を鏡面に加工したもの ( $\text{Ra}=0.3$ ) を用いて表1に示す様な理想条件にする以外は、実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0097】実施例6

トナーに第二の無機微粉体M-1を0.1部添加する以外は実施例5と同様の方法で評価を行なった。結果を表1に示す。

【0098】実施例7

トナーに第三の無機微粉体M-1を0.1部添加する以外は実施例5と同様の方法で評価を行なった。結果を表1に示す。

【0099】実施例8

第一無機微粉体として、L-2 ( $\text{pH}=6.3$ 、濃密度 $=165\text{g}/\text{リットル}$ ) を1.5部添加する以外は実施例1と同様の方法でトナー ( $X=5.8\mu\text{m}$ 、 $Y=1$

7.5%) を得た。以下実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0100】実施例9

トナー担持体としてPMAA粒子 (固数平均径 $6.5\mu\text{m}$ ) 15部をさらに添加する以外は実施例1と同様の方法で作製した $\text{Ra}=1.5$ のトナー担持体を用いる以外は実施例1と同様の方法で評価を行なった。但しトナーは $X=5.8\mu\text{m}$ 、 $Y=17.5\%$ のものを用いた。以下実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0101】実施例10

実施例1と同様の方法でトナー ( $X=5.3\mu\text{m}$ 、 $Y=23\%$ ) を得た。以下実施例1と同様の方法で評価を行なった。結果を表1に示す。

【0102】比較例1

トナー担持体として、PMAA粒子 (固数平均径 $6.5\mu\text{m}$ ) 25部をさらに添加する以外は、実施例1と同様の方法で作製した $\text{Ra}=2.5$ のコーストスリプを用いた。第一無機微粉体としては、L-4 ( $\text{pH}=3.0$ 、濃密度 $=35\text{g}/\text{リットル}$ ) を1.0部添加し、トナー粒径は $X=7.8\mu\text{m}$ 、 $Y=4.0\%$ のものを使用し、トナーの製法及び評価法に関しては実施例1と同様の方法で行なった。結果を表1に示す。

【0103】比較例2

トナー担持体として、実施例5で用いたものと同様のものを用いた。無機微粉体としてはL-4を1.2部添加し、トナー粒径は $X=5.1\mu\text{m}$ 、 $Y=31.0\%$ のものを使用した。トナーの製法及び評価法に関しては実施例1と同様の方法で行なった。結果を表1に示す。

【0104】

【表1】

